Evaluation of High-Pressure, High-Temperature Inorganic Hydrogen Membranes

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ABSTRACT

A membrane reactor with the capability of high-pressure, high-temperature hydrogen permeation testing has recently been fabricated at the National Energy Technology Laboratory (NETL). The interest in high-pressure, high-temperature inorganic membrane evaluation stems from the elevated process environments where hydrogen is produced (for example, synthesis gas production), as well as the increase in a membrane's permeability that can be obtained under such conditions. Permeability experiments have been conducted at NETL with 1mm-thick palladium membranes under high pressures (101 to 3102 kPa / 14.7 to 450 psi) and temperatures (623 to 1173 K) to verify the performance of the membrane reactor. Elevated pressure and temperature tests have also been conducted in the evaluation of a novel cermet membrane provided by Argonne National Laboratory (ANL).

The hydrogen permeability of palladium was found to be proportional to the relation of the partial pressure gradient of hydrogen across the membrane to the n^{th} power, or $\Delta P_{H2}^{0.59}$ for this study. Moreover, the permeability data collected for the palladium membrane were described by an Arrhenius-type expression where 3.54E-7 mol H_2 $m^{-1}s^{-1}Pa^{-0.59}$ and 16.13 kJ mol^{-1} represent the pre-exponential factor and the activation energy respectively. The permeability results obtained for the palladium membrane, using the NETL reactor are in good agreement with literature values.

Preliminary tests have also been carried out with an ion-transport cermet membrane. Cermet membranes composed of mixed oxides and metallic nickel, fabricated by ANL, were tested under conditions similar to those used for the palladium membrane. The cermet membrane experiments resulted in permeability values approximately one order of magnitude lower than those of the palladium membranes. The testing of bulk and palladium coated refractory metals, new cermet compositions, porous ceramics and other novel composites are currently underway at the NETL research facilities.

Introduction

Environmental concerns and regulations are the incentives for the technological advancement of clean fuels as we embark on the 21st century. These motivations have propelled industry and the U.S. government to invest a large amount of resources in alternative fuel research (fuel cells, Fischer-Tropsch synthesis, hydrogen, etc). Hydrogen has a great deal of potential in clean fuel technology, both directly, as a combustible fuel, and/or indirectly in fuel cell applications. An environmental advantage of hydrogen is that it burns cleaner than conventional fuels, with water being the primary product upon combustion in air. However, hydrogen separation and purification has been identified as a bottleneck in the development of advanced hydrogen fuel technologies. Many techniques for hydrogen separation are in use or are currently being investigated, such as cryogenic separation, pressure swing adsorption, catalytic purification and selective diffusion (Grashoff, et al. 1983). Ion- and atomic-transport membranes, selective to only one species, are the sub-categories of selective diffusion technology which are of interest in this study.

Recently, NETL has designed and constructed a testing unit for hydrogen separation studies. The construction of the hydrogen membrane testing (HMT) unit gives NETL the ability to evaluate membranes at relatively high pressures and temperatures. The HMT unit was constructed for the purpose of analyzing the diffusion of hydrogen through different membrane materials at pressures and temperatures up to 450 psi at 900^{o}C. An upgrade to the HMT unit is currently underway at NETL that will allow the evaluation of the effect of hydrogen membranes on the kinetics of reactions such as the water-gas shift reaction and the steam reforming of light hydrocarbons.

Many metals, such as palladium and a selection of the refractory metals, have shown high diffusion capabilities with respect to hydrogen. Palladium was selected as the membrane material for the verification of the NETL membrane reactor performance because of the extensive hydrogen permeability data found in literature. Experiments with hydrogen permeable palladium membranes began in the middle of the 19th century by researchers including Deville, Troost, and Graham. As a result of its high hydrogen permeability, good mechanical characteristics and highly catalytic surface which dissociates hydrogen rapidly, palladium is still the membrane material of choice in many applications. Unfortunately, palladium and its alloys are extremely expensive, roughly twice the cost of gold, making them impractical for large-scale applications. Therefore, an economically feasible, palladium based, commercial scale system would require a significantly reduced amount of palladium, which can be accomplished by techniques such as thin palladium membranes supported on porous substrates (Ueimya, et al. 1991, Itoh, et al. 1992) or highly permeable bulk substrates (Buxbaum and Kinney, 1996). The high cost of palladium has turned the attention of researchers to palladium-free membrane technologies, such as cermets and ceramics for high-pressure, high-temperature applications.

Experimental Section

A high-pressure, high-temperature HMT unit has recently been constructed at NETL where permeability experiments have been conducted using several membrane materials. The membranes tested were of a disk configuration, approximately 0.04 inches (1mm) thick and 0.625 inches in diameter. The membrane disks were mounted into a predetermined length of 0.75 inches O.D. Inconel 600 tubing using a brazing method developed by NETL for the bulk metals or by ANL for the cermet membranes. Inconel 600 was chosen as the material of construction for the reactor's heated zone because of its high temperature strength, while 316 stainless steel was used for the bulk of the reactor construction. Inconel tubes, 0.375 inches in diameter, were placed concentrically inside the 0.75 inches tubing approximately 0.25 inches from the membrane surface. The "tube inside a tube" configuration, as shown in Figure 1, allowed for the feed and sweep gases to enter the reactor, contact the membrane, and exit the reactor on both the retentate and permeate sides of the membrane.

The membrane reactor was encased in a two-gallon stainless steel autoclave, which was purged with nitrogen. The reactor feed gas consisted of a known concentration of hydrogen with the balance being helium, while the sweep gas feed was

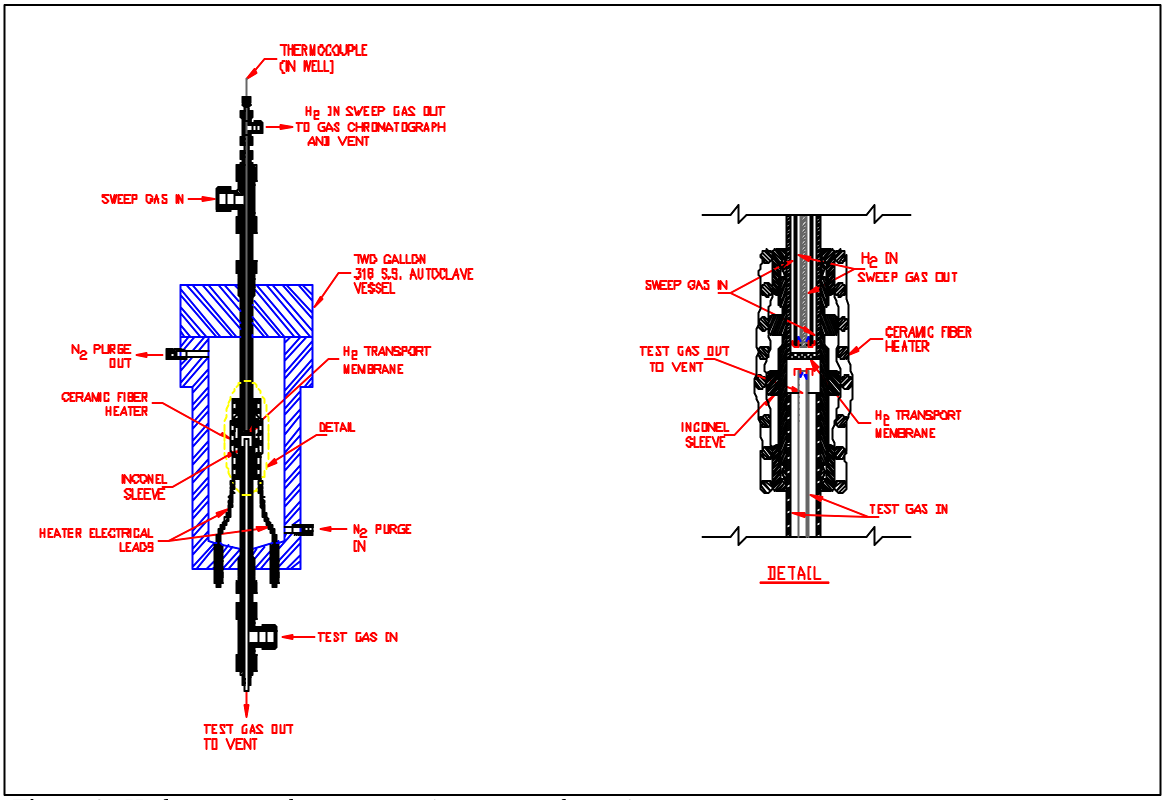

Figure 1. Hydrogen membrane reactor/separator schematic.

composed of 100% argon. The selection of a feed gas mixture of hydrogen/helium was made to simplify the detection of any leaks that may have developed in the reactor system while testing. While the helium and hydrogen molecules are very similar in size, only the hydrogen molecule has the ability to pass through the membranes via ionic- or atomic-diffusion. Thus, any detection of helium in the sweep or permeate would indicate a reactor or membrane leak. The temperature of the system was maintained with a 6-inch ceramic fiber heater and measured using type-K thermocouples, which were placed 0.25 inches from one or both surfaces of the membrane.

The feed gas was introduced to the reactor at a flow rate sufficient to ensure that the hydrogen concentration at the membrane surface was not depleted by permeation through the membrane. Hydrogen permeating through the membrane was carried to a Hewlett Packard 5890 Series II Gas Chromatograph (GC) by the argon sweep stream. The argon sweep stream flow rate was regulated to maintain the hydrogen concentration within the calibration range of the GC. An excessively large flow rate would result in a hydrogen concentration below the GC detection limit of approximately 20-ppm, while an insufficient flow rate would result in saturation of the GC detector. CHROM Perfect GC analysis software was used for GC control and data collection. The hydrogen partial pressure and hydrogen flux through the membrane could be determined from the measured hydrogen concentrations, and flow rates of the retentate and permeate streams, as well as the accessible surface area of the membrane.

Three membrane materials were tested in the described apparatus, two bulk metals and one novel cermet composition. Palladium foil, of 99.99% purity, was tested and compared to reported literature values for hydrogen/palladium permeation for the verification of the data collected for the membrane configuration. Because most metals are permeable to hydrogen, tests were also performed on Inconel 600 to evaluate the influence of the reactor's material of construction on the permeance testing of other membranes. The cermet membrane tested was provided by Argonne National Laboratory and designated as ANL-1. The ANL-1 membrane's fabrication and composition ($BaCe_{0.80}Y_{0.20}O_3$ with nickel metal) is described elsewhere (Enick et al. 2000).

Hydrogen permeation experiments were conducted at various pressures and temperatures. The temperatures ranged from 673 K to 1173 K and the pressures ranged from atmospheric to 450 psia. A typical test procedure involved stepping pressure up and down under isothermal conditions, and then repeating the pressure changes under a new isothermal temperature condition. An example of typical hydrogen flux data illustrating the flux response to pressure and temperature changes is shown in Figure 2. Inert gas was used for the reactor heat up to avoid the exposure of the membrane to hydrogen during the α-,β-phase transition temperature (300^{o}C) of palladium (Grashoff, et al. 1983). It should also be noted that ample time was allowed for the system to equilibrate after changes in reactor pressure and temperature.

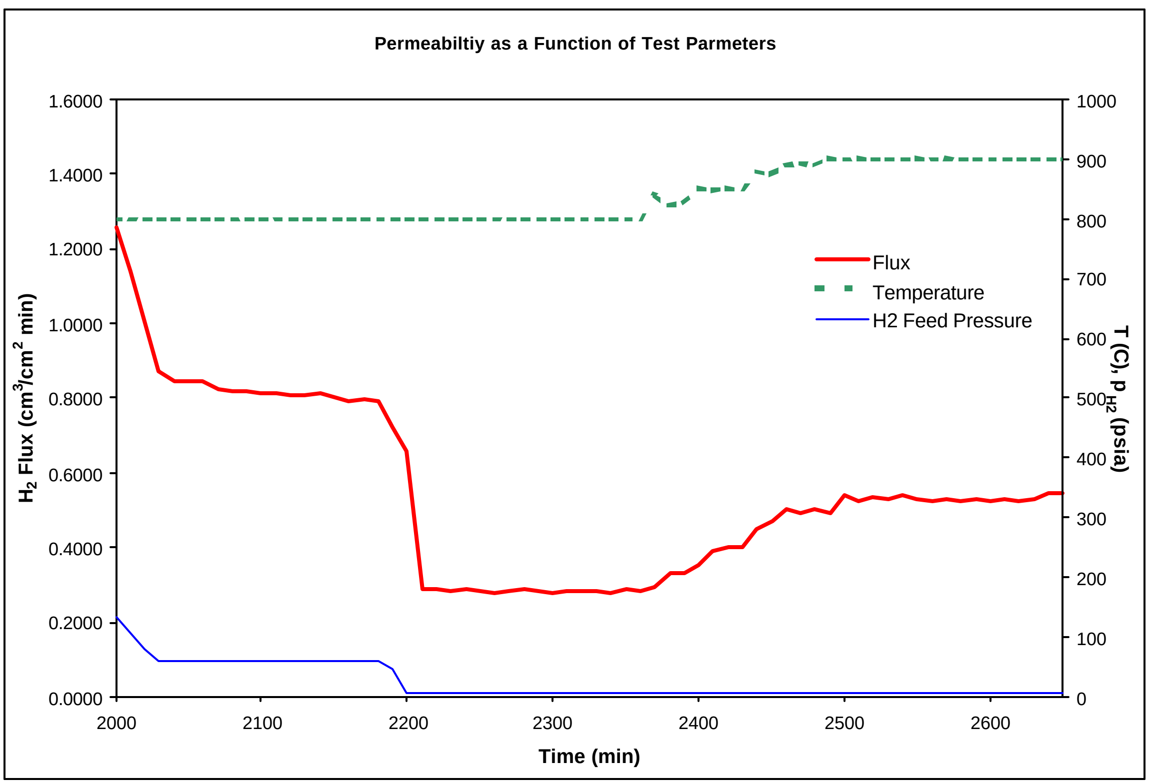

Figure 2. Hydrogen flux as a function of test parameters, T and P.

The hydrogen flux through the membrane is represented by Equation 1 as a function of hydrogen partial pressure, the permeability constant of the membrane material and the thickness of the membrane, X_M. The driving force for hydrogen permeation through the membrane is directly proportional to the difference in the hydrogen partial pressures of the retentate and permeate, each to the n^{th} power. Because of the effects of internal and external mass transfer in the diffusion mechanism through the membrane, the hydrogen partial pressure power, n, may not represent the common value for ion- or atomic transport, 0.5 (Hsieh, 1996). The membrane permeability, k, and the partial pressure exponent, n, were calculated by using a linear, best-fit line through the hydrogen flux and the difference in the hydrogen partial pressures to the n^{th} power. The resulting plot yielded the permeability constant, as well as the partial pressure power by their relation to the intercept and the slope respectively.

$$N_{H2} = -k \frac{\left(P^n_{H2,Ret} - P^n_{H2,Per}\right)}{X_M} \tag{1}$$

Results & Discussion

Preliminary high-pressure, high-temperature membrane testing has recently been conducted at the NETL Hydrogen Membrane Technology (HMT) facility to verify the performance of the recently constructed membrane reactor. The results of this membrane testing are given in Table 1.

Membrane Composition	**Membrane Thickness** (microns)	**T** (K)	$P_{Tot, Ret}$ (kPa)	$P_{H2, Ret}$ (kPa)	$P_{Tot, Per}$ (kPa)	$P_{H2, Per}$ (kPa)	**n**	**k** (mol H_2/m s Pa^n)
Palladium	1000	623	101-2757	91-2840	118	0	0.62	1.63E-8
Palladium	1000	723	101-2757	91-2840	118	0	0.61	2.47E-8
Palladium	1000	908	101-2757	91-2840	118	0	0.57	3.58E-8
Palladium	1000	1038	101-2757	91-2840	118	0	0.57	5.55E-8
Palladium	1000	1173	101-2757	91-2840	118	0	0.57	7.38E-8
ANL-1	1200	973	101-1880	101-1880	115	0	0.53	4.93E-9
ANL-1	1200	1073	101-1860	50-911	115	0	0.53	1.11E-8
ANL-1	1200	1173	101-790	50-387	115	0	0.55	1.92E-8
Inconel 600	1100	873	1503-2930	1503-2930	117	0	0.65	1.05E-10
Inconel 600	1100	973	101-2930	101-2930	117	0	0.48	1.25E-10
Inconel 600	1100	1073	101-2930	101-2930	117	0	0.40	2.74E-10
Inconel 600	1100	1173	101-2930	101-2930	117	0	0.45	5.55E-10

Table 1. Summary of the permeability characteristics of the membrane testing at NETL.

The integrity of the membrane unit constructed at NETL was accomplished through the comparison of literature and experimental values of hydrogen diffusion through palladium. The agreement between the literature values (Koffler, et al. 1969) and the experimental results is illustrated in Figure 3.

Since most metals are permeable to hydrogen, testing was also conducted to determine the effect of the permeance of the reactor's material of construction, Inconel 600, on the permeability collected on tested membranes. The permeation results of the Inconel 600 reactor material indicated permeation values between 1 and 10% as compared to the palladium and the cermet membrane data. Although the flux through the Inconel 600 reactor had some effect on the permeation values obtained, adjustments to the palladium and ANL-1 membrane permeability data were considered negligible at this time. This assumption was considered suitable because of the complexity in the mass transfer of hydrogen as a result of the configuration and geometry of the system.

As expected, hydrogen permeation data showed a strong dependence on pressure and temperature. In addition, selectivity to only hydrogen was also verified for all tested membranes materials under the experimental conditions. As is evident from Table 1 and illustrated by Figure 3, an increase in temperature of the membrane resulted in an increase in the permeation for all of the membrane materials. The temperature dependence of the membrane permeability, k, is also represented in a best-fit Arrenhius form by Equations 2, 3, and 4 for palladium, ANL-1 and the Inconel 600 membrane data respectively.

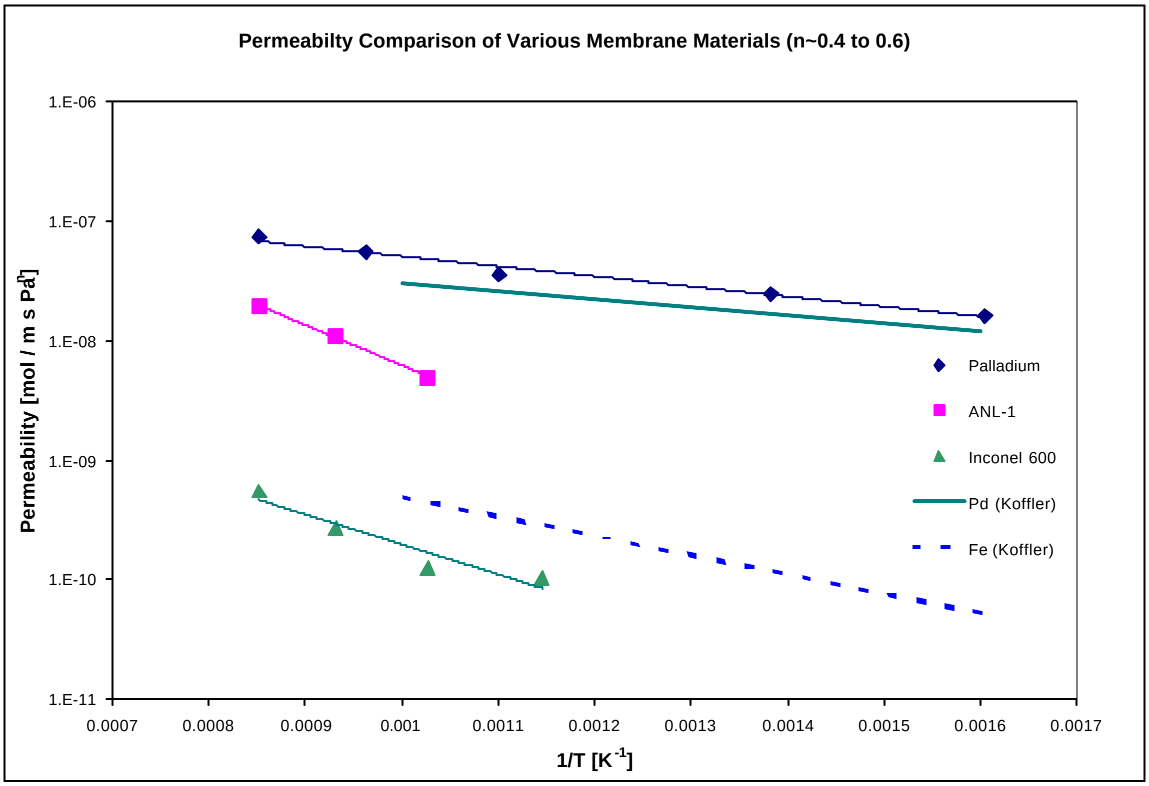

Figure 3. Permeability comparion of tested membrane materials with that of selected literature values.

$$k_{Pd} = 3.54E-7 \exp\left(\frac{-16.13}{RT}\right) \equiv \left[\frac{mol}{m\ s\ Pa^{0.59}}\right] \tag{2}$$

$$k_{ANL-1} = 1.5E-5 \exp\left(\frac{-64.68}{RT}\right) \equiv \left[\frac{mol}{m\ s\ Pa^{0.54}}\right] \tag{3}$$

$$k_{Inc600} = 6.4E-8 \exp\left(\frac{-47.97}{RT}\right) \equiv \left[\frac{mol}{m\ s\ Pa^{0.50}}\right] \tag{4}$$

An increase in hydrogen permeation was also demonstrated by increasing the hydrogen partial pressure differential across the membrane during flux testing. An example of the pressure and temperature effects on hydrogen flux data are illustrated in Figure 2.

The ANL-1 membrane also showed the same partial pressure and temperature dependence as was demonstrated by the palladium. However, the permeation values obtained for the ANL-1 membrane were approximately one order of magnitude lower than for those of palladium. Moreover, the duration of testing of any individual ANL-1 membrane did not surpass 70 hours due to the development of leaks in the membrane assembly. Inspection of the membranes after testing indicated that leakage typically was due to failure of the cermet to metal seal and not the membrane material itself.

Conclusion

The agreement, illustrated in Figure 3, between the literature and experimental values measured for hydrogen diffusion through palladium demonstrated that the recently constructed high-pressure, high-temperature reactor functioned efficiently. The relationship also provides confidence in the results of presently tested membrane materials, as well as future membrane tests conducted at NETL.

The high-pressure, high-temperature palladium membrane testing demonstrated a high permeability and 100% selectivity to hydrogen, as well as a highly catalytic surface to hydrogen dissociation under the experimental conditions. Permeation values obtained illustrate the effectiveness that palladium membranes can have in high-pressure, high-temperature, hydrogen separation technology. Nevertheless, due to the high price of palladium, alternatives must be sought which reduce the amount of palladium needed to construct an economically feasible membrane reactor. A technique to retain the highly effective properties of palladium while decreasing the membranes total palladium content is the deposition of thin layers of palladium on the surface of porous substrates or on highly permeable refractory metals. The refractory metals, zirconium, tantalum, and vanadium all have permeation rates greater than that of palladium and are inexpensive compared to palladium. These metals, however, lack the mechanical attributes and/or the catalytic surface needed for hydrogen dissociation (Buxbaum and Marker, 1993).

The ANL-1 membrane provided by ANL and tested at the NETL facility exhibited good preliminary permeation characteristics for use in membrane processes. Although the membranes permeability is lower than palladium, ANL is in the process of developing improved cermet compositions. The 0.04 in. (1mm) thick ANL-1 membrane exhibited good mechanical integrity, withstanding temperatures up to 900^{c}C and pressure differentials of 400 psi. However, quality improvements to the cermet to metal seal is an area where further work is required.

Nomenclature

N_{H2}	Hydrogen flux.
k	Membrane permeability constant.
$P_{H2,Ret}$	Hydrogen partial pressure of the retentate or feed stream.
$P_{H2,Per}$	Hydrogen partial pressure of the permeate or "product" stream.
n	Partial pressure exponent.
X_M	Membrane thickness.
$P_{Tot,Ret}$	Total pressure of the retentate or feed stream.
$P_{Tot,Per}$	Total pressure of the permeate or "product" stream.
k_z	Permeability constant of material Z.
R	Gas constant.
T	Temperature.

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